

2D electron-hole condensate at a germanium surface

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A condensation of electron-hole pairs in a 2D electron-hole condensate has been observed at a germanium surface with a high density of surface states.

A new photoluminescence line, the "S line," was detected in germanium in Ref. 1. This line results from a radiative recombination of spatially separated 2D layers of electrons and holes which are localized near a semiconductor-electrolyte interface. Such a system can exist if a quantum well for equilibrium charge carriers is produced by an external electric field applied to the surface of the semiconductor. The system is characterized by a repulsive interaction between electron-hole pairs.^{2,3} An increase in the density of pairs in the system leads to an increase in their energy and to a short-wave shift of the S emission line.^{1,3}

In the present letter we wish to examine another possibility for the formation of a 2D electron-hole system. This possibility stems from the existence of a high density of surface states. We will show that in this case the formation of the system may be accompanied by a condensation of electron-hole pairs at the surface.

The optical excitation of a surface with centers of concentration M results in a charge exchange of these centers and in the appearance of a nonequilibrium surface charge N_s , which sets up an electric field in the semiconductor. If N_s is sufficiently large, and the relation $\gamma_e > \gamma_h$ holds (more on this below), a quantum well for holes forms at the surface and in turn gives rise to a second well, this one for electrons^{2,3} (Fig. 1). Under the assumption that there are surface states of only one type, the value of N_s in the steady state is determined by the equation

$$\frac{dN_s}{dt} = \gamma_e(M - N_s)N_e - \gamma_h N_s(N_e + N_s) = 0, \quad (1)$$

where $\gamma_{e,h} = \sigma_{e,h}v_{e,h}$ are the trapping coefficients for electrons and holes, $N_h = N_e + N_s$, and N_e is the density of electron-hole pairs in surface quantum wells. From (1) we find

$$N_s = -\frac{1}{2}N_e(1 + \gamma_e/\gamma_h) + \sqrt{\frac{1}{4}N_e^2(1 + \gamma_e/\gamma_h)^2 + MN_e\gamma_e/\gamma_h}. \quad (2)$$

We see that a uniform charge distribution along the surface would be unstable in this case. Let us examine the energy of the ground state of a pair:

$$E_g = \frac{1}{N_e} \int_0^{N_e} \mu(N_e) dN_e \quad (3)$$

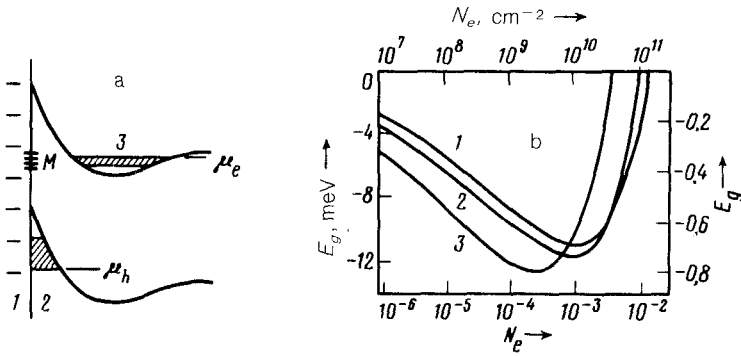


FIG. 1. a: Band diagram of a germanium surface with surface centers in a concentration M during photoexcitation. 1—Charge of surface centers; 2—hole quantum well; 3—electron quantum well. b: Ground-state energy of the electron-hole pairs for a $\langle 100 \rangle$ germanium surface versus the density of these pairs for various concentrations of surface states, M (cm⁻²). 1— 5×10^{12} ; 2— 1×10^{13} ; 3— 5×10^{13} , $\gamma_e/\gamma_h = 10^2$, $m_z^h = 0.3 m_0$, $m_{dh} = 0.4 m_0$, $m_z^e = 0.12 m_0$, $m_{de} = 0.3 m_0$, $\nu_h = 1$, $\nu_e = 4$, $T = 0$ K. The scales at the left and at the bottom are in Bohr units for holes: Ry and z_h^{-2} , where $r_h = \hbar^2/(e^2 m_z^h)$.

(μ is the chemical potential of the pair). An expression for this energy can be derived easily in the approximation $N_e \ll M$ and $\gamma_e > \gamma_h$, in which case we have, according to (2), $N_s \approx (N_e M \gamma_e / \gamma_h)^{1/2} \gg N_e$. We assume that the particles are in quantum wells in their ground states and can be described by variational wave functions⁴ $\Psi_{h,e}(z) = (b_{h,e}^3/2)^{1/2} z \exp(-b_{h,e}z/2)$. In this approximation, $b_h \ll b_e$, the overlap of wave functions is slight, and the quantum wells may be regarded as independent of each other, so that the surface charge for the first well is $\approx N_s$, while that for the second well is the excess concentration of holes in the first well, equal to N_e . The variational parameters $b_{h,e}$ are then given by

$$b_h = \left(\frac{33}{2} \pi \frac{e^2 m_z^h N_s}{\epsilon \hbar^2} \right)^{1/3}, \quad b_e = \left(\frac{33}{3} \pi \frac{e^2 m_z^e N_e}{\epsilon \hbar^2} \right)^{1/3}, \quad (4)$$

where $m_z^{e,h}$ are the masses of the charge carriers along the z axis, which runs perpendicular to the surface. For μ we find

$$\mu \approx -0.1 \hbar^2 \left(\frac{b_h^2}{m_z^h} - 6 \frac{b_e^2}{m_z^e} \right) - 0.54 \frac{e^2}{\epsilon} (N_s b_h)^{1/3} - \frac{e^2 b_e}{8\epsilon} + \pi \hbar^2 \left(\frac{N_s}{\nu_h m_{dh}} + \frac{N_e}{\nu_e m_{de}} \right). \quad (5)$$

The first term here describes the energy of the ground level of holes and electrons in the Hartree approximation⁴; the second describes the exchange energy found for the holes in the model of a local density⁵; the third describes the energy of electron-hole correlations, thought of as the energy of the interaction of electrons with their image in the first layer²; and the last describes the Fermi energy of the particles in the wells. From (3)–(5) we find

$$E_g = -0,3 \hbar^2 \left(\frac{1}{4} \frac{b_h^2}{m_z^e} - \frac{6}{5} \frac{b_e^2}{m_z^e} \right) - 0,44 \frac{e^2}{\epsilon} (N_s b_h)^{1/3} - \frac{3}{32} \frac{e^2 b_e}{\epsilon} + \pi \hbar^2 \left(\frac{2}{3} \frac{N_s}{v_h m_{dh}} + \frac{1}{2} \frac{N_e}{v_e m_{de}} \right). \quad (6)$$

Figure 1 shows a plot of $E_g(N_e)$. The fact that there is an energy minimum means that a stable stationary state corresponds to a partitioning of the system into regions consisting of 2D electron-hole layers in which the density of pairs is constant and corresponds to a minimum of their free energy in the region in which there are not quantum walls. This phenomenon may be thought of as a condensation of electron-hole pairs at the surface.⁶ It should be manifested as a constancy of the shape and position of the S line in the face of changes in the excitation level.

The case of a high density of surface states has been arranged by etching germanium in nitric acid at a concentration below 10N, at which the density of surface states can reach $\approx 10^{13} \text{ cm}^{-2}$, according to Ref. 7. We used p -type germanium in the experiments; the experimental procedure is the same as described in Ref. 1.

Figure 2 shows photoluminescence spectra of the germanium surface. A characteristic feature of these spectra is the presence of two new lines, S_2 and S_3 , which can be separated by virtue of a difference in the behavior of their intensities as functions of the excitation level (Fig. 3). The positions and shapes of the lines are essentially

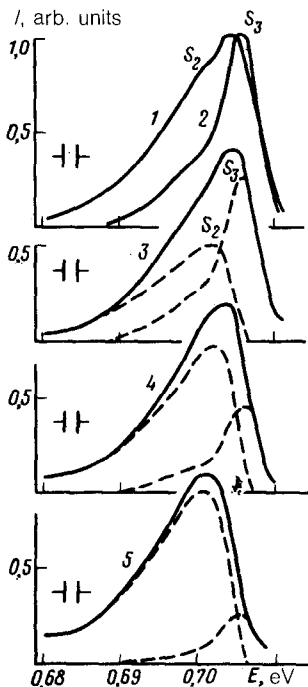


FIG. 2. Emission spectra of a germanium (100) surface after etching in HNO_3 at various concentrations (1—1N; 2—3N; 3—5—7N) at various excitation levels G (W/cm^2): 1—3—1.25; 4—0.32; 5—0.1. Lines S_2 and S_3 contain LA and TO components ($T = 4.2 \text{ K}$).

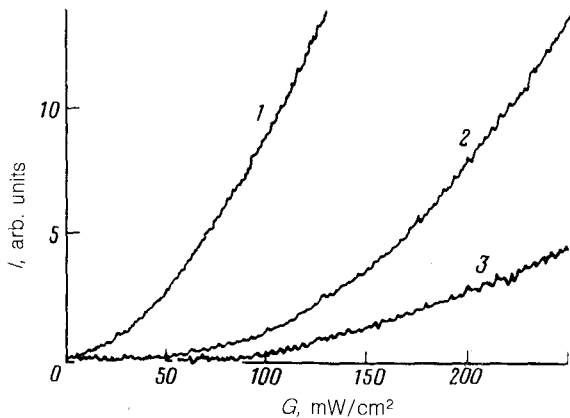


FIG. 3. Dependence of the exciton emission intensity ($h\nu = 0.714$ eV)— S_3 line ($h\nu = 0.707$ eV) (2) and S_2 line ($h\nu = 0.690$ eV) on the excitation level for a germanium $\langle 100 \rangle$ surface etched in $1N$ HNO_3 .

independent of the excitation level. The relative intensity of line S_2 correlates with the behavior of the surface-state density as a function of the HNO_3 concentration which was found in Ref. 7: It reaches a maximum at $1N$ and $7N$, where we have $M \sim 10^{13}$ cm^{-2} , and it is slightly lower at $3N$, with $M \sim 10^{12}$ cm^{-2} .

For the interfaces studied, there is typically a weak surface field which rules out the formation of an equilibrium quantum well at the germanium surface. Nevertheless, the shape and spectral position of line S_2 are approximately the same as those for the line S which was observed in Ref. 1 for the structure germanium- $14NHNO_3$ under conditions such that there was a substantial band curvature, corresponding to the appearance of a p -type conduction channel, but the density of surface states was low ($M \sim 10^{11}$ cm^{-2}). This results suggests that line S_2 stems from 2D electron-hole layers which arise as a result of a charge exchange of surface centers with $\gamma_e > \gamma_h$ and which exist as a 2D condensate with a constant pair density. This conclusion is supported by the threshold in the appearance of line S_2 in the spectrum as the excitation level is raised (Fig. 3).

The spectral position of line S_3 , in contrast with that of S_2 , does not depend on the particular electrolyte used or on the orientation of the crystal surface. This line exists at $T \lesssim 10$ K; it also appears once a threshold exciton density is reached (Fig. 3). It may be that S_3 is due to an electron-hole liquid which is localized near the surface, trapped in a shallow surface potential well created by the surface band curvature. From the spectral position and width of the line we can estimate the binding energy of the excitons in the surface electron-hole liquid: $\varphi_0 \approx 4$ MeV.

The surface condensation of electron-hole pairs, which has been observed previously in III-V and II-VI semiconductors,⁶ can apparently be described by the model discussed here.

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